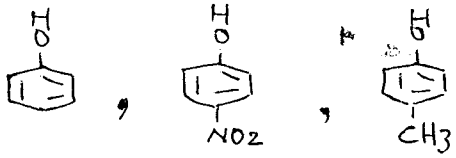
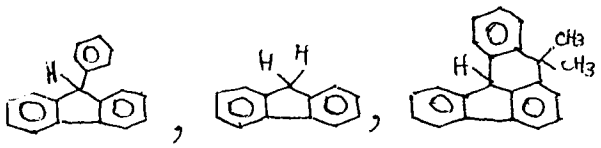
1) List the realtive ordering of acidity in each set and explain it.

a) (10 %)

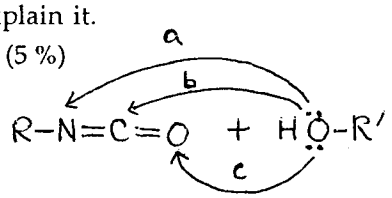


b) (10 %)

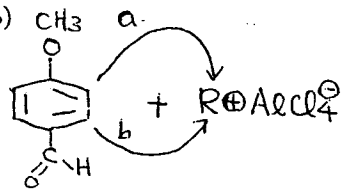


2) In the following reactions, there are different possible reaction pathways (a, b or c). Please indicate which of the pathway is the most probable one in each set and explain it.

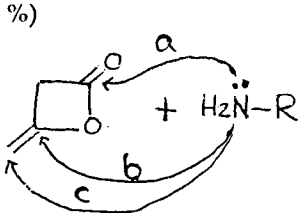
a) (5 %)



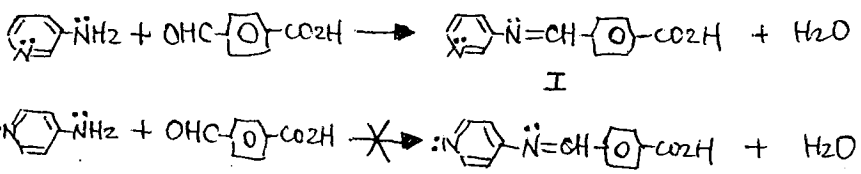
b) (5 %)



c) (5 %)

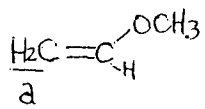


3) a) Reaction a can proceed easily while reaction b failed to react. Give a probable reason for it. (12 %)

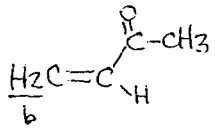


b) Compound I generated from reaction a above possesses several intermolecular interactions due to its specific chemical structure. What are them? (8 %)

4) a) Which of the vinyl proton (a or b) in the two compounds below has the higher chemical shift (in δ value)? (5 %) why? (7 %)



a



b

b) Resolve the chemical structures based on the following spectroscopic data.

i) Molecular formula: $C_{12}H_{18}$ (6 %)

$^1H$ NMR, δ: 2.2 singlet

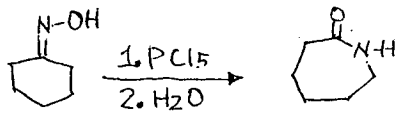
ii) Molecular formula: $C_7H_{16}O_3$ (6 %)

$^1H$ NMR, δ 1.2 triplet (9H); δ 3.6 quartet (6H); δ 5.1 singlet (1 H)

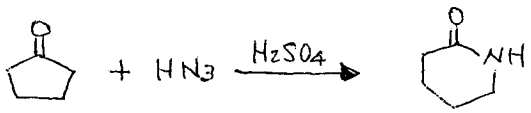
5) Show the detailed mechanistic steps involved in the following rearrangements.

a) Iodoform test (7 %)

b) Beckmann rearrangement (7 %)



c) Schmidt rearrangement (7 %)



（橫書式） 國立中山大學 八十五 學年度碩博士班招生考試試題

科 目：物理化學 材料所 甲組



1. Three sets of diatomic molecules are given below.
   Series A: HF, HCl, HBr, and HI  Series B: $F_2$, $Cl_2$, $Br_2$, and $I_2$  Series C: CO and NO
   (1) In general, how many modes of fundamental vibration do we expect for each series of molecules? Specifically, what are the expected modes? Explain. [6%]
   (2) For a given fundamental mode, rank the vibration frequency in decreasing order within EACH series. Explain reasons behind your ranking. [12%]

2. Prove the identity that $(\partial P/\partial V)_T = -(\partial P/\partial T)_V / (\partial V/\partial T)_P$. Is this relationship universally true to any system or there are cases where this equation may become inapplicable? Explain. [12%]

3. The equation of van der Waals is often written as $(P+\mathbf{a}/V^2)(V-\mathbf{b}) = RT$ where V is the molar volume of the gas. Compared to the ideal gas law (i.e., PV = RT), there are two additional terms (i.e., $\mathbf{a}/V^2$ and $-\mathbf{b}$) in the van der Waals equation. What are the physical meanings of these two terms? In addition, give your own rationalization as to why there should be a factor of $V^{-2}$ associated with the parameter **a**. [15%]

4. At a common reduced temperature $T_r$ (= T/T* where * denotes critical point), experimental data from different gases for the variation of the compressibility factor z = PV/RT with $P_r$ = P/P* fall on a single curve as may be observed from Figure 1. This is a remarkable manifestation of the law of corresponding state.
   (1) What is the molecular origin of this principle of corresponding state? Why were critical properties (P*, V*, and T*) used as the reference parameters? [10%]
   (2) Note from Figure 1 that, for a given $T_r$, z decreases first to reach a minimum and then increases with increasing $P_r$. This is generally true and is more apparent when $T_r$ is relatively low. In your opinion, what is the molecular origin of this behavior? [10%]

5. It is well known that added electrolytes tend to decrease the solubility of nonelectrolytes in a polar solvent such as water. Give your explanation to this well-known "salting out" effect. [15%]

6. The Beer-Lambert law states that the absorbance $A = \ln(\mathbf{I_0}/\mathbf{I})$ (where $\mathbf{I_0}$ and **I** are respectively the intensities of the incident and the transmitted beam) is linearly related to the length of the light path **b** and the concentration of the absorbing species **c**, i.e., $A = \varepsilon\mathbf{bc}$ in which the proportional constant $\varepsilon$ is called the extinction coefficient. Derive this equation yourself. Explain clearly your model and state explicitly the assumptions made. [20%]

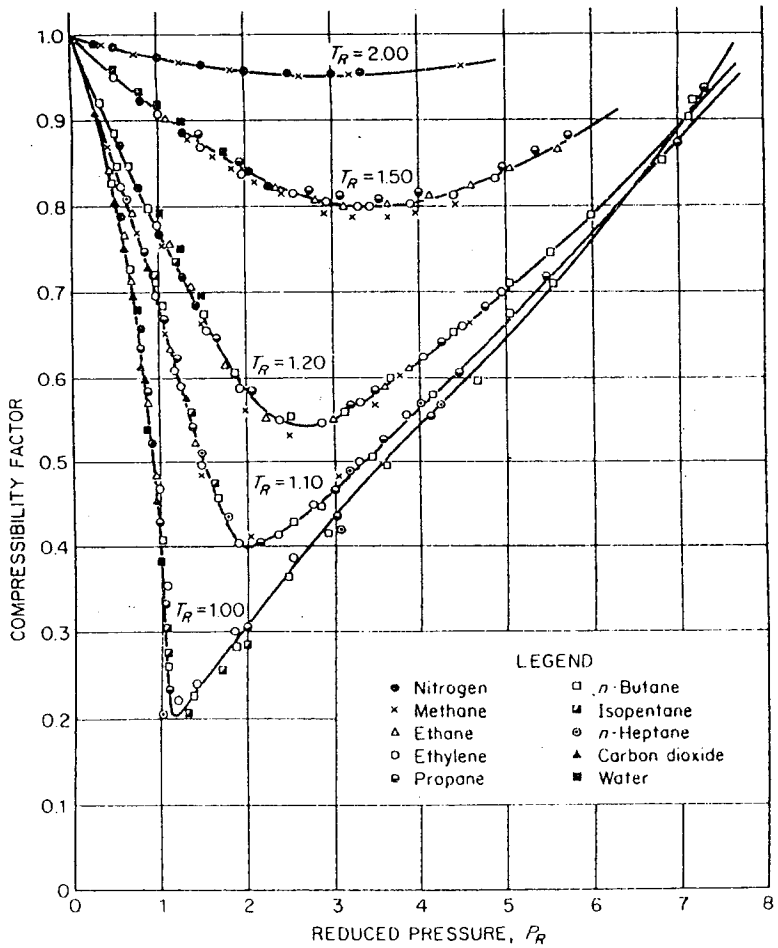



FIG. 1. Compressibility factor as function of reduced state variables. [Gouq-Jen Su, *Ind. Eng. Chem.*, 38, 803 (1946)].

25% for each problem

1. Two cylindrical rods, one made of steel ($E_S$=200 GPa) and the other of brass ($E_b$=105 GPa), are joined at C. End A of the composite rod obtained in this way is fixed, while a 0.12-mm gap exists between end E and a vertical wall. A 60-kN force is then applied at B and a 40-kN force at D, both horizontal and directed to the right (as shown in Fig. 1). Determine (a) the reactions at A and E, (b) the deflection of point C.

2. The following readings have been obtained from a strain rosette attached to the surface of a machine component (Fig. 2):

$$\varepsilon_1 = -57.5 \times 10^{-6} \text{ in./in.}, \quad \varepsilon_2 = -57.5 \times 10^{-6} \text{ in./in.},$$
$$\varepsilon_4 = +220 \times 10^{-6} \text{ in./in.}$$

(a) What should be the reading of gage 3? (b) Determine the principal strains and the maximum shearing strain. (Use $\upsilon = 0.3$)

3. For the truss and loading shown (Fig. 3, A and 2A are cross section area), determine the horizontal and vertical deflection of joint C.

4. A plane stress state $\sigma_x = -3$ ksi, $\sigma_y = -12$ ksi, $\tau_{xy} = 18$ ksi occurs in a machine component made of a steel with $\sigma_Y = 36$ ksi. Determine whether yield occurs using (a) the maximum-shearing-stress criterion, (b) the maximum-distortion-energy criterion.

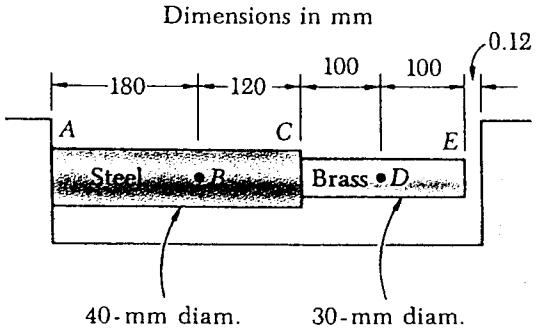



Fig. 1

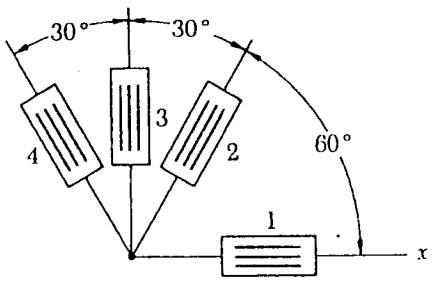



Fig. 2

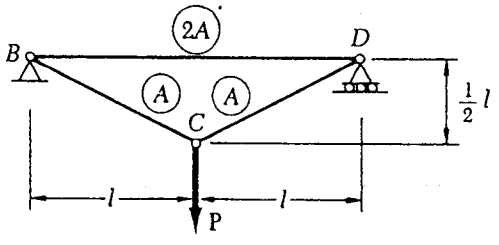



Fig. 3

（橫書式） 國立中山大學八十五學年度碩博士班招生考試試題

科 目：工程數學(材料科學研究所)乙,丙組 共二頁 第一頁

1、請解下列之微分方程

（a）$x^2\frac{d^2y}{dx^2}+5x\frac{dy}{dx}+4y=0 \qquad x>0$ (7%)

（b）$(3xy+y^2)+(x^2+xy)\frac{dy}{dx}=0$ (7%)

（c）$\frac{d^4y}{dx^4}+y=0$ (7%)

2、

（a）若一函數定義為 $f(t)=\begin{cases}0 & t<1\\ t^2-2t+2 & t\geq 1\end{cases}$ 請求出 Laplace transform (6%)

（b）若一函數為 $F(s)=\frac{e^{-2s}}{s^2+s-2}$ 請求inverse Laplace transform(6%)

3、請利用複變數之方法求得下列之積分值

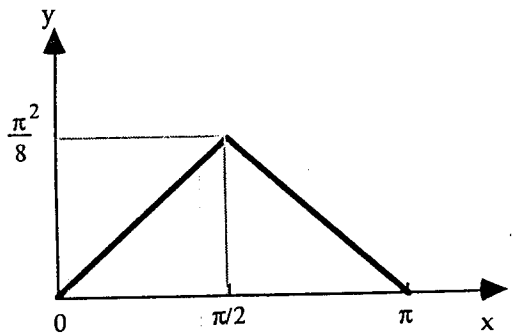
（a）$\int_0^\infty \frac{x^{\alpha-1}dx}{1+x} \qquad 0<\alpha<1$(8%)

（b）$\int_0^\infty \frac{\sin x^2}{x}$ (8%)

4、任一據有週期性之函數皆可以三角函數之級數表示之，其表示方法如下

$$f(x)=A_o+\sum_{n=1}^{\infty}[a_n\cos nx+b_n\sin nx]$$

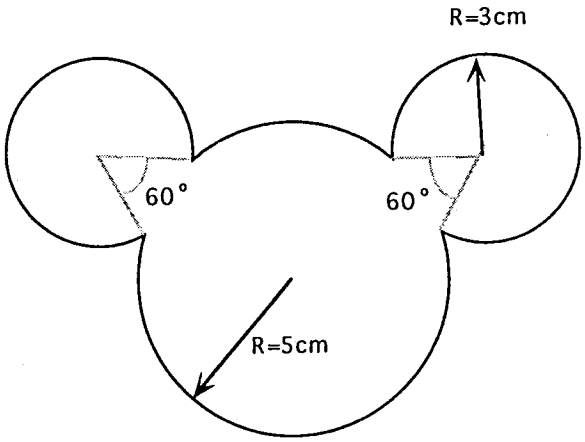
請將下列之波形以此種方式表示出來 (20%)



5、請計算下列矩陣的eigenvalues 以及eigenvectors (10%)

$$A=\begin{pmatrix}0 & 1 & 1\\ 1 & 0 & 1\\ 1 & 1 & 0\end{pmatrix}$$

6、迪士奈公司的主角乃是家喻户曉的米老鼠，現下面有一米老鼠的外貌，請問這個圖形的周長爲多少？而其面積爲多少？若有一天米老鼠想送一個具有心形的巧克力蛋糕給他的女朋友請問這塊蛋糕的體積有多大？(21%)
心形的曲線方程式如下：
$f(\theta)=20(1-\cos\theta)$（單位：公分）其厚度爲10公分。




參考公式

(1) $\int x^n \sin ax\ dx=-\frac{x^n}{a}\cos ax+\frac{x}{a}\int x^{n-1}\cos ax\ dx$

(2) $\int x^n \cos ax\ dx=\frac{x^n}{a}\sin ax-\frac{x}{a}\int x^{n-1}\sin ax\ dx$

(3) $\mathrm{L}\{f(t)\}=F(s)=\int_0^\infty e^{-st}f(t)dt$

1. Methane($CH_4$) is delivered at 298 K to a glass factory, which operates a melting furnace at 1600 K. The fuel is mixed with a quantity of air, also at 298 K, which is 10% in excess of the amount theoretically needed for complete combustion.( Air is approximately 21% $O_2$ and 79% $N_2$).

(a) Calculate the heat of reaction of Methane($CH_4$) with oxygen at 298 K, assuming that the products of reaction are $CO_2$ and $H_2O$(gas).(10%)

(b) Assuming complete combustion, what is the composition of the flue gas(the gas following combustion)?(10%)

(c) What is the temperature of the gas, assuming no heat loss?(15%)

Data: $\Delta H^{\circ}_{298}$, $CH_4$ (g) = -17.89 kcal/(g.mol)
$\Delta H^{\circ}_{298}$, $CO_2$ (g) = -94.05 kcal/(g.mol)
$\Delta H^{\circ}_{298}$, $H_2O$ (g) = -57.80 kcal/(g.mol)

Cp, $CH_4$ (g) = 16.0 cal/(mol.K)
Cp, $CO_2$ (g) = 13.7 cal/(mol.K)
Cp, $H_2O$ (g) = 11.9 cal/(mol.K)
Cp, $N_2$ (g) = 8.2 cal/(mol.K)
Cp, $O_2$ (g) = 8.2 cal/(mol.K)

2. (a) What is the enthalpy of pure, liquid aluminum at 1000 K?(use pure, solid aluminum at 298 K as the reference state)(10%)

(b) An electric resistance furnace is used to melt pure aluminum at the rate of 100 kg per hour. The furnace is fed with solid aluminum at 298 K. The liquid aluminum leaves the furnace at 1000 K. What is the minimum electric power rating (kW) of the furnace?(10%)

Data for aluminum:
atomic weight = 27 g/mol
heat capacity of solid = 26 J/(mol.K)
heat capacity of liquid = 29 J/(mol.K)
melting point = 932 K
heat of fusion = 10700 J/mol

3. Calculate $\Delta U$ and $\Delta S$ when 0.5 mol of liquid water at 273 K is mixed with 0.5 mol of liquid water at 373 K. and the system is allowed to reach equilibrium in an adiabatic enclosure. Assume that $C_p$ is 77 J/(mol.K) from 273 K to 373 K.(15%)

4. Compute the entropy difference between 12 kg of water at 40 °C and 12 kg of ice at -10 °C.(15%)

Data: Cp,water = 4.184 J/g.K; Cp,ice = 2.1 J/g.K;
Heat of melting of ice is 336 kJ/kg

5. (a) The isotopic composition of lead, in atoms percent, is $^{204}Pb$, 1.5%; $^{206}Pb$, 23.6%; $^{207}Pb$, 22.6%; $^{208}Pb$, 52.3%. Calculate the entropy of mixing per mole of Pb at a temperature of 0 K.(10%)

(b) The Third Law states that $S^{o} = 0$ at 0 K. How do you rationalize the difference between your calculation and the Third Law?(5%)